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9500536.9 **11 January 1995 (11.01.95)** **GB**(71) Applicant (for AU BB CA GB IE KE LK LS MN MW NZ SD SG SZ TT UG only): **UNILEVER PLC (GB/GB); Unilever House, Blackfriars, London EC4P 4BQ (GB).**(71) Applicant (for all designated States except AU BB CA GB IE KE LK LS MN MW NZ SD SG SZ TT UG): **UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).**(72) Inventors: **ARAYA, Abraham; 53 Friars Close, Bebington, Wirral, Merseyside L63 3HY (GB). CHAPPLE, Andrew, Paul; Glasfryn Cottage, Ffordd Uchaf, Gwynfryn, Near Wrexham, Clwyd LL11 5UN (GB). MADDISON, Christopher; 9 Childer Crescent, Little Sutton, South Wirral, Cheshire L66 1RE (GB).**(81) Designated States: **AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).****Published***With international search report.**Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*(54) Title: **PARTICLES CONTAINING PERFUME**

(57) Abstract

Perfume is absorbed onto aluminosilicate of the zeolite P type having a silicone to aluminium ratio not greater than 1.33. The zeolite of this type also functions as a detergency builder when the detergent composition is used.

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PARTICLES CONTAINING PERFUME

This invention relates to perfume-containing
5 particles suitable for use in fabric laundering detergent
compositions.

Background of the Invention and Summary of the Prior Art

There have been a number of proposals for
10 absorbing perfume onto a solid carrier material, and
various reasons for doing so. In a number of instances,
the objective of such proposals has been merely to
convert liquid perfume into a solid form which can more
readily be incorporated into another product. It has
15 been asserted that such carrier substances may serve to
protect the perfume from loss during storage or protect
it from contact with other constituents of a composition.

Examples of disclosures of such carriers for
perfume are GB-A-1306924, US-A-3449266, US-A-3909461, US-
20 A-4536315, US-A-4539135, US-A-4713193, GB-A-2066839, EP-
A-332259, EP-A-332260 and JP-A-63/79662.

EP-A-535942 and EP-A-536942 are concerned with
carrier materials which serve to reduce the vapour
pressure of absorbed perfume.

25 As pointed out in those documents, a carrier
material which reduces the perfume vapour pressure over
the solid carrier but releases the perfume on contact
with water can be useful when perfuming a concentrated

laundry detergent composition or fabric softening composition.

These concentrated products are used in relatively small quantity by the consumer and therefore
5 need to contain a higher concentration of perfume than is otherwise customary, in order to provide a normal quantity of perfume when added to a wash or rinse liquor for use. However, the presence of such an enhanced concentration of perfume in such products can give them
10 an unpleasantly strong odour. As disclosed in the above mentioned European published application, the use of a carrier material which reduces the vapour pressure of the perfume can serve to reduce the perfume odour of the product to a satisfactory level, whilst still providing
15 the desired quantity of perfume in a wash liquor or rinse liquor at the time of use.

Another possible utilisation of carriers which reduce the vapour pressure of perfume is to permit a change in fragrance when the laundry detergent or fabric
20 softening composition is added to water to form a wash or rinse liquor. To achieve this, some perfume ingredients would be absorbed onto the carrier while others were not. Until the composition is added to water at the time of use, the perfume constituents on the carrier would have
25 their vapour pressure and consequent perceptibility reduced relative to the other ingredients which were not so absorbed.

In these prior disclosures, the carrier

substance has generally been a material which was inert. It was desirable to achieve a high loading of perfume onto the carrier solid so as to keep to a minimum the quantity of carrier solid which was required.

5 Our EP-A-535942, teaches that the carrier material should have a substantial volume of pores, having a pore diameter in a range from 7 to 50 angstroms.

Materials which can fulfil this criterion are some silicas and zeolite Y. Zeolite Y does not have
10 sufficient ion exchange capacity for use as a detergency builder. By contrast, zeolite 4A which does sufficient have ion exchange capacity and is useful as a detergency builder, does not fulfil this criterion for a volume of pores in the size range 7 to 50 angstroms. A comparative
15 example in EP-A-535942 shows that zeolite 4A can serve as a carrier for perfume, but gives only a small reduction in the vapour pressure of the perfume even in the absence of other ingredients of a detergent composition.

Our EP-A-384070 published on 29 August 1990
20 discloses another type of zeolite which is able to function as a detergency builder. It is a form of zeolite P, more specifically it is defined in EP-A-384070 as alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than
25 1.33, preferably not greater than 1.15. This material can be called "maximum aluminium zeolite P", or "zeolite MAP". A preferred process for making it is the subject of EP-A-565364.

Summary of the Invention

We have found that this zeolite MAP can serve as a useful carrier for perfume. Although it does not meet the pore size/volume requirements of our EP-A-535942 mentioned above, we have surprisingly found that if the concentration of perfume on this zeolite is kept within a modest range, a reduction in perfume vapour pressure is obtained.

Because the zeolite can itself be incorporated in a detergent composition in substantial amounts in order to function as a detergency builder, and thus perform a useful function in the wash liquor, it is useful as a perfume carrier even though the concentration of perfume on the zeolite is not high.

Broadly, therefore, according to a first aspect of this invention, there is provided alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, and having perfume absorbed thereon in a quantity not exceeding 8% by weight of the said aluminosilicate.

Zeolite MAP used to carry perfume and which is to be mixed with other constituents of a detergent composition may already be mixed with some other materials. Often these will be only a minority of the material present, until the zeolite MAP is mixed into the detergent composition. An aspect of the invention may therefore be defined as a particulate composition which comprises alkali metal aluminosilicate of the zeolite P

type having a silicon to aluminium ratio not greater than 1.33, as more than 50% by weight of the composition and perfume absorbed thereby in a quantity which is from 0.2% to 8% by weight of the said aluminosilicate, and
5 optionally a minority of other constituents. Thus, the aluminosilicate may provide from 50 to 99.8% of this composition.

In a second aspect this invention provides a particulate detergent composition containing from 2 to
10 60% by weight of detergent active and from 5 to 60% by weight of the alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, and from 0.1 to 3% of perfume absorbed on the said aluminosilicate, the weight of perfume being not
15 more than 8% of the weight of the said aluminosilicate.

When such a detergent composition is made, by mixing other ingredients with the aluminosilicate which has perfume absorbed thereby, the resulting composition will exhibit a greater concentration of perfume on the
20 aluminosilicate than in the remainder of the composition.

In a third aspect, this invention provides a method of making a particulate detergent composition which comprises

- (i) absorbing perfume onto alkali metal
25 aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33,
- (ii) subsequently, mixing the said aluminosilicate and absorbed perfume thereon with other ingredients of

the composition including detergent active, the amount of said perfume being from 0.2 to 8% by weight of aluminosilicate of the said type in the detergent composition.

5 In yet another aspect, this invention provides use of alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33 as a carrier material to incorporate perfume into a detergent composition and reduce the vapour pressure of
10 the perfume.

Further Description and Embodiments

As is well known, a perfume normally consists of a mixture of a number of perfumery materials, each of
15 which has a fragrance. The number of perfumery materials in a perfume is typically ten or more. The range of fragrant materials used in perfumery is very wide; the materials come from a variety of chemical classes, but in general are hydrophobic oils. In many instances, the
20 molecular weight of a perfumery material is in excess of 150, but does not exceed 300.

Although the invention is not limited to specific perfumery materials, some perfumery materials which may be used include: acetyl cedrene,
25 4-acetoxy-3-pentyltetrahydropyran, 4-acetyl-6-t-butyl-1,1-dimethylindane, available under the trademark "CELESTOLIDE",
5-acetyl-1,1,2,3,3,6-hexamethylindane, available under

the trademark "PHANTOLIDE",
6-acetyl-1-isopropyl-2,3,3,5-tetramethylindane, available
under the trademark "TRASEOLIDE",
alpha-n-amylcinammic aldehyde, amyl salicylate, aubepine,
5 aubepine nitrile, aurantion,
2-t-butylcyclohexyl acetate, 2-t-butylcyclohexanol,
3-(p-t-butylphenyl)propanal,
4-t-butylcyclohexyl acetate,
4-t-butyl-3,5-dinitro-2,6-dimethyl acetophenone,
10 4-t-butylcyclohexanol, benzoin siam resinoids,
benzyl benzoate, benzyl acetate,
benzyl propionate,
benzyl salicylate, benzyl isoamyl ether,
benzyl alcohol, bergamot oil, bornyl acetate,
15 butyl salicylate, carvacrol, cedar atlas oil,
cedryl methyl ether, cedryl acetate, cinnamic alcohol,
cinnamyl propionate, cis-3-hexenol,
cis-3-hexenyl salicylate, citronella oil, citronellol,
citronellonitrile, citronellyl acetate,
20 citronellyloxyacetaldehyde, cloveleaf oil, coumarin,
9-decen-1-ol, n-decanal, n-dodecanal, decanol,
decyl acetate, diethyl phthalate, dihydromyrcenol,
dihydromyrcenyl formate, dihydromyrcenyl acetate,
dihydroterpinyl acetate,
25 dimethylbenzyl carbonyl acetate, dimethylbenzylcarbinol,
dimethylheptanol, dimethyloctanol, dimyrcetol, diphenyl
oxide,
ethyl naphthyl ether, ethyl vanillin,

- ethylene brassylate, eugenol, geraniol, geranium oil,
geranonitrile, geranyl nitrile, geranyl acetate,
1,1,2,4,4,7-hexamethyl-6-acetyl-1,2,3,4-
tetrahydronaphthalene, available under the trademark
5 "TONALID",
1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-2-
benzopyran, available under the trademark "GALAXOLIDE",
2-n-heptylcyclopentanone,
3a,4,5,6,7,7a-hexahydro-4,7-methano-1(3)H-inden-6-
10 ylpropionate, available under the trademark
"FLOROCYCLENE",
3a,4,5,6,7,7a-hexahydro-4,7-methano-1(3)H-inden-6-
ylacetate, available under the trademark "JASMACYCLENE",
4-(4'-hydroxy-4'-methylpentyl)-3-cyclohexenecarbaldehyde,
15 alpha-hexylcinammic aldehyde, heliotropin, Hercolyn D,
hexyl aldol, hexyl cinnamic aldehyde,
hexyl salicylate, hydroxycitronellal, i-nonyl formate,
3-isocamphylcyclohexanol, 4-isopropylcyclohexanol,
4-isopropylcyclohexyl methanol, indole, ionones, irones,
20 isoamyl salicylate, isoborneol,
isobornyl acetate, isobutyl salicylate, isobutylbenzoate,
isobutylphenyl acetate, isoeugenol, isolongifolanone,
isomethyl ionones, isononanol, isononyl acetate,
isopulegol, lavandin oil,
25 lemongrass oil, linalool, linalyl acetate, LRG 201,
1-menthol, 2-methyl-3-(p-isopropylphenyl)propanal,
2-methyl-3-(p-t-butylphenyl)propanal,
3-methyl-2-pentyl-cyclopentanone,

- 3-methyl-5-phenyl-pentanol,
alpha and beta methyl naphthyl ketones, methyl ionones,
methyl dihydrojasmonate, methyl naphthyl ether,
methyl 4-propyl phenyl ether, Mousse de chene Yugo,
- 5 Musk ambrette, myrtenol, neroli oil,
nonanediol-1,3-diacetate, nonanol, nonanolide-1,4, nopol
acetate,
1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethyl-2-acetyl-
naphthalene, available under the
- 10 trademark "ISO-E-SUPER",
octanol, Oppoponax resinoid, orange oil,
p-t-amylcyclohexanone,
p-t-butylmethylhydrocinnamic aldehyde,
2-phenylethanol, 2-phenylethyl acetate,
- 15 2-phenylpropanol, 3-phenylpropanol, para-menthan-7-ol,
para-t-butylphenyl methyl ether, patchouli oil,
pelargene, petitgrain oil, phenoxyethyl isobutyrate,
phenylacetaldehyde diethyl acetal,
phenylacetaldehyde dimethyl acetal,
- 20 phenylethyl n-butyl ether, phenylethyl isoamyl ether,
phenylethylphenyl acetate, pimento leaf oil,
rose-d-oxide, Sandalone, styrallyl acetate,
1,1,4,4-tetramethyl-6-acetyl-7-ethyl-1,2,3,4-
tetrahydronaphthalene, available under the trademark
- 25 "VERSALIDE",
3,3,5-trimethyl hexyl acetate,
3,5,5-trimethylcyclohexanol,
terpineol, terpinyl acetate, tetrahydrogeraniol,

tetrahydrolinalool, tetrahydromuguol, tetrahydromyrcenol,
thyme oil, trichloromethylphenylcarbonyl acetate,
tricyclodecenyl acetate, tricyclodecenyl propionate,
10-undecen-1-al, gamma undecalactone, 10-undecen-1-ol
5 undecanol, vanillin, vetiverol, vetiveryl acetate,
vetyvert oil,
acetate and propionate esters of alcohols in the list
above, aromatic nitromusk fragrances, indane musk
fragrances, isochroman musk fragrances, macrocyclic
10 ketones, macrolactone musk fragrances, and tetralin musk
fragrances.

Perfumes frequently include solvents or
diluent, for example: ethanol, isopropanol, diethylene
glycol monoethyl ether, dipropylene glycol, diethyl
15 phthalate and triethyl citrate.

Perfumes which are used in this invention may,
if desired, have deodorant properties as disclosed in US-
A-4303679, US-A-4663068 and EP-A-545556.

Forms of zeolite having the required properties
20 to be useful in the present invention are disclosed in
EP-A-384070 referred to above, the disclosure of which is
incorporated herein by reference. As stated in that
document, such forms of zeolite are of the zeolite P type
and have Si:Al ratios not greater than 1.33, i.e. the
25 quantity of Si is not more than 1.33 times the quantity
of Al. They have good calcium binding capacities,
usually at least 150 mg CaO, preferably at least 160 mg
CaO, per gram anhydrous aluminosilicate. The Si:Al ratio

preferably lies within the range of from 0.9 to 1.33,
more preferably from 0.9 to 1.2.

The aluminosilicates used in the present
invention are in alkali metal salt form. The preferred
5 cation is sodium.

It is desirable that the zeolite MAP has a small
particle size. Desirably the average particle size is
less than 4 micrometres. Desirably also, at least 90% by
weight of the zeolite MAP has a particle size less than
10 7, better less than 5 micrometres.

A process for the preparation of zeolite MAP
suitable for use in this invention is described in
EP-A-565364.

The amount of perfume will generally be at least
15 0.5% by weight of the zeolite MAP. Up to at least 8% by
weight of the zeolite, there is a trade off between the
amount of perfume carried by the zeolite and the
reduction in vapour pressure. In order to give more
substantial reduction in vapour pressure it is preferred
20 that the quantity of perfume is not more than 6%, better
not more than 5% by weight of the zeolite. Preferably,
the quantity of perfume is at least 1% and frequently at
least 2% by weight of the zeolite.

Absorption of perfume onto the zeolite MAP can
25 be carried out simply by mixing the perfume with the
zeolite, possibly followed by a period of storage to
allow equilibrium distribution to be obtained.

The amount of detergent active to be

incorporated in a detergent composition of this invention lies in the broad range from 2% to 60% by weight.

Surfactants useful as detergent active in the detergent compositions herein include well-known anionic, 5 nonionic, amphoteric and zwitterionic surfactants.

Typical of these are the alkyl benzene sulphonates, alkyl sulphonates, allyl- and alkyl ether sulphates, primary alkyl sulphates, alkoxylated alcohols, alpha-sulphonates of fatty acids and of fatty acid esters, alkyl betaines, 10 and polyalkyl glycosides all known in the detergent art.

Detergent active is preferably present in a quantity of at least 5% or 10% by weight of a composition, and may well be in a quantity not exceeding 50% or 40% by weight. Concentrated detergent 15 compositions will generally contain detergent active in a quantity from 10% to 50% by weight of the composition.

The specified zeolite MAP provides from 5 to 60% of a detergent composition of this invention. The amount may be at least 10% and may lie in a range not exceeding 20 40% by weight. It may be the only zeolite present, or it may be used jointly with zeolite A. Generally if zeolite A is also present the total quantity of zeolite is not more than 80%, better 60% by weight of the composition.

The zeolite may be accompanied by a co-builder. 25 Preferred are organic polymers containing carboxylate groups, especially co-polymers of maleate and acrylate. Such polymers may usefully be used in amounts from 1% to 10% by weight of the detergent composition.

Other detergency builders may also be present, notably the conventional inorganic and organic water soluble builder salts. Examples are alkali metal carbonates, borates, phosphates, polyphosphates, tripolyphosphates, bicarbonates, silicates, sulphates, and citric acid salts. The builder is preferably present at a total level not exceeding 80%, more preferably not over 60% by weight.

A detergent composition may include bleaches, notably peroxyacids such as diperoxydodecanedioic acid or phthaloylaminoperoxypropionic acid, or bleach systems that comprise a peroxide compound with liberates hydrogen peroxide in aqueous solution and an activator. Hydrogen peroxide sources are well known in the art, and include compounds such as alkali metal perborates, percarbonates, persulphates and persilicates, and urea peroxide; particularly percarbonate.

Preferred bleach activators are N,N,N,N-tetraacetylenediamine (TAED), 1,2,3,4,6-pentaacetylglucose (GPA), sodium-p-acetoxylbenzenesulphonate (SABS), sodium-p-benzoyloxybenzenesulphonate (SBOBS), sodium-p-nonanoyloxybenzenesulphonate (SNOBS), sodium-p-3,5,5-trimethylhexanoyloxy-benzenesulphonate (iso-SNOBS), 2-N,N,N-trimethylammonioethyl-4-sulphophenylcarbonate (CSPC), and transition metal catalysts disclosed in EP-A-458397, EP-A-458398 and EP-A-549272.

Other ingredients which may optionally be

present in a detergent composition include fabric softening agents such as fatty amines, fabric softening clay materials, lather depressants, and, usually present in very minor amounts, fluorescent agents, perfumes including deodorant perfumes, enzymes such as proteases, cellulases, amylases and lipase, germicides and colorants.

Detergent compositions of this invention will generally be in solid form, e.g. granular products commonly referred to as powders.

Preferably, a detergent composition is made by the method which is an aspect of this invention in which the perfume is absorbed on zeolite MAP, after which this zeolite MAP is mixed with other ingredients of the composition.

In this procedure, it is possible to mix perfume with only part of the zeolite MAP which is present in the final composition. If so, the perfume absorbed on zeolite MAP might, for a time, exceed 8% of the weight of zeolite which is carrying it. When this zeolite MAP is mixed into the rest of the composition including more zeolite MAP, the proportion of perfume relative to the overall quantity of zeolite MAP will of course then fall. The proportions should be arranged so that the amount of perfume is not over 8% by weight of the total quantity of zeolite MAP.

It is also possible to obtain the reduction in vapour pressure of perfume even when the perfume is added

to a detergent composition which has already been prepared from its constituted materials.

Examples

5 Example 1

Zeolite MAP was produced as described in EP-A-565364. Its micropore volume, that is to say pores in the approximate range 7 to 50 angstroms, was measured by the nitrogen absorption methods referred to in EP-A-10 535942, and found to be less than 0.02 ml/g.

Its volume of pores of larger size was then determined by mercury porosimetry and found to be 0.9 ml/g.

Particle size was determined using a Malvern 15 Mastersizer instrument. Average size was found to be 0.9 μm with about 60% of particles in the range 0.6 to 1 μm .

A number of samples of this zeolite MAP were used to absorb varying concentrations of a perfume composition intended for the perfuming of fabric washing detergent 20 products. To absorb the perfume, a weighed quantity of perfume was poured onto a weighed quantity of the zeolite MAP in a glass screw top bottle. The contents were then mixed by stirring with a glass rod or stainless steel spatula until the mixture showed no signs of free liquid 25 or "wet" lumps. More zeolite was then added with constant stirring until the required perfume to zeolite ratio was reached. The bottle was then sealed and roller mixed for several days to equilibrate the sample.

Occasionally during this time any solid lumps were broken up by manual stirring.

The quantity of perfume in the headspace over the zeolite was determined by gas chromatographic headspace analysis. A 1 g sample of the zeolite was placed in a 20 ml crimped top vial, and allowed to equilibrate for one hour at 60°C. The headspace was then analysed using a Perkin Elmer HS 101 headspace auto-sampler linked to a Perkin Elmer 8500 gas chromatograph. The column used was 2 metres of Carbowax 20M (polyethylene glycol, average MW 15,000-20,000) on Chromosorb W.HP (white diatomaceous earth) available from Hewlett Packard. Results are quoted as the total peak area.

Samples prepared and analysed in this way contained 2%, 5%, 10% and 20% of perfume by weight of zeolite MAP. A comparison was carried out using zeolite 4A. The results obtained were:

Perfume concentrations	Peak area zeolite MAP	Peak area zeolite 4A
2%	45	190
5%	140	
10%	220	230
20%	220	

These results show that 10% perfume saturates the zeolite MAP, so that there is no vapour pressure reduction. At 2% and 5% however, the vapour pressure of

perfume was 20% and 64% of the vapour pressure at saturation. By context, zeolite 4A was almost saturated at 2% concentration. Thus at concentrations below 10%, the zeolite MAP is much more effective than zeolite 4A in
5 reducing perfume vapour pressure.

Example 2

Samples of the two zeolites, each carrying 2% perfume, were added to equal values of distilled water.
10 The perfume in the head space was then measured by gas chromatography as in the previous example.

There was very little difference in the peak areas, indicating complete release of the perfume on contact with water.

15

Example 3

The above results were confirmed by a panel test. 0.5 g of zeolite MAP or of zeolite 4A, carrying in either case absorbed perfume at a concentration of 2% by
20 weight based on the zeolite, were placed in 50 ml screw top jars and allowed to equilibrate for 1 hour at 27°C.

Two jars, one of each were then presented to each of 11 panellists who were asked to decide which contained the stronger perfume. This experiment was
25 repeated twice, The panellists unanimously picked the jars containing zeolite MAP as having the weaker perfume, thus indicating the greater ability of zeolite MAP to absorb and retain perfume.

Example 4

A quantity of zeolite MAP was divided into two portions. One was made to absorb 2% perfume, as in Example 1.

5 0.70g samples of each zeolite were weighed into separate 500ml aliquots of a solution containing 0.01M sodium chloride and 3.92×10^{-3} M calcium chloride, maintained at 25°C. The calcium ion exchange capacity was determined after 30 minutes by immersing a calcium
10 sensitive electrode in the solution.

The values obtained were 159 mg/gram for zeolite which did not carry perfume and 157 mg/gram for the zeolite which did carry perfume. The difference in these values was not significant. It was thus confirmed that
15 zeolite MAP could be used as a perfume carrier in a detergent composition and then function as a detergency builder when the composition is added to water at the time of use.

Example 5

Two detergent compositions were prepared containing:

	parts by weight
5 coconut alkyl sulphate	8
nonionic surfactant (C ₁₃ alcohol 7EO)	9
zeolite	35
sodium carbonate	10
10 sodium stearate 2	
acrylic maleic copolymer (Sokolan CP5)	2
sodium carboxymethyl cellulose	1
15 perfume	0.7

[These compositions were models for a product containing 8% anionic detergent, 9% nonionic, 35% zeolite and 0.7% perfume, and including a bleach system]

20

In one composition the zeolite was zeolite 4A in the other it was zeolite MAP. In both cases the perfume was 2% of the weight of zeolite and was absorbed on the zeolite, as in Example 1, before adding the zeolite to
25 the remainder of the composition.

Gas chromatography was used to measure the concentration of perfume in the headspace over the detergent composition, using the same procedure as in Example 1.

It was found that the intensity of the perfume over the composition containing zeolite 4A was 10% greater than over the composition containing zeolite MAP, indicating that zeolite MAP retains its ability to absorb and retain perfume even when incorporated into a detergent composition with nonionic detergent present.

The intensity of perfume in the headspace over the two compositions was also assessed by a panel, with a procedure as in Example 3, placing 3g of one or other composition in the 50ml screw topped jars. A total of 99 assessments was made by the panel who decided by a ratio of 2:1 that the perfume over the composition containing zeolite MAP was weaker.

15 Example 6

A perfume containing more than 10 fragrance materials was absorbed onto zeolite MAP by the procedure of Example 1. Samples of the mixture were then stored in sealed jars at room temperature for 3 months.

20 After this time the perfume remaining in the composition was extracted with solvent and analysed by gas chromatography. It was found that 68% of the original quantity of perfume remained and that chromatography peaks corresponding to many of the original fragrance materials were still present.

25

Example 7

A granular detergent composition is prepared to the following formulation:

5		%
	Linear alkylbenzene sulphonate	25.0
	Nonionic Surfactant	1.5
	Soap	1.0
	Zeolite MAP (anhydrous)	35.0
10	Perfume	1.0
	Sodium silicate	4.0
	Acrylic maleic copolymer	1.5
	Fluorescer	0.18
	Sodium carboxymethyl cellulose	0.6
15	Sodium Carbonate	14.3
	Enzyme (Alcalase (Trade Mark))	0.6
	Antifoam	0.04
	Alusil N (finely divided silica flow aid)	2.5
20	Other minor ingredients	balance to 100%

The perfume is carried on the zeolite MAP, and is thus present at a concentration of approximately 3% by weight based on the zeolite.

The composition is prepared by absorbing all the perfume on one quarter (or alternatively one half) the zeolite MAP, and mixing this into the remainder of the detergent composition - which may itself be prepared by mixing the ingredients or else by spray drying those ingredients which are not sensitive to heat, and mixing

in the others.

Example 8

A granular detergent composition is prepared to
5 the following formulation:

		%
	Linear alkylbenzene sulphonate	6.6
	Tallow alkyl sulphate	2.4
10	Nonionic surfactant (C ₁₃ alcohol 7EO)	6.1
	Zeolite MAP (anhydrous)	22
	Perfume	0.8
	Sodium silicate	2.7
	Polyacrylate	5.6
15	Sodium perborate tetrahydrate	14.0
	Tetraacetyl ethylene diamine (TAED)	6.1
	Fluorescer	0.5
	Sodium carboxymethyl cellulose	0.5
	Sodium carbonate	17.3
20	Enzyme (Savinase (Trade Mark))	1.6
	Silicone antifoam	0.16
	Sodium sulphate, water and other minor ingredients	balance to 100%

25 The perfume is carried on the zeolite MAP, and
is thus again present at a concentration of approximately
3% by weight based on the zeolite. This composition can
be prepared in the same way as for the preceding example.

CLAIMS:

1. A particulate composition which comprises
 - (i) more than 50% by weight of alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, and
 - (ii) perfume absorbed thereby in a quantity which is from 0.2% to 8% by weight of the said aluminosilicate.
2. A particulate composition according to claim 1 wherein the ratio of Si to Al in the said aluminosilicate lies in a range from 0.9:1 to 1.15:1.
3. A particulate composition according to claim 1 or claim 2 wherein the amount of perfume is from 0.5 to 8% by weight of the said aluminosilicate.
4. A particulate composition according to claim 1 or claim 2 wherein the amount of perfume is from 0.5 to 6% by weight of the said aluminosilicate.
5. A particulate detergent composition comprising:
 - 2 to 60% by weight of detergent active,
 - 5 to 60% by weight of alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, and
 - 0.1 to 3% by weight perfume which is at least partly

absorbed on the said aluminosilicate, the weight of perfume being not more than 8% of the weight of the said aluminosilicate.

6. A particulate detergent composition according to claim 5 wherein the amount of perfume is from 0.5 to 8% by weight of the said aluminosilicate.

7. A method of making a particulate detergent composition comprising 2 to 60% by weight of detergent active, 5 to 60% by weight of alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33, and 0.1 to 3% by weight perfume, which method comprises

i) absorbing perfume onto alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33,

ii) mixing the said aluminosilicate and absorbed perfume thereon with other ingredients of the composition including detergent active, the amount of said perfume being from 0.2 to 8% by weight of aluminosilicate of the said type in the detergent composition.

8. A method according to claim 7 wherein the amount of perfume is from 0.5 to 8% by weight of the said aluminosilicate.

9. A method according to claim 7 wherein the amount of

perfume is from 0.5 to 6% by weight of the said aluminosilicate.

10. Use of alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not greater than 1.33 as a carrier material to incorporate perfume into a detergent composition and reduce the vapour pressure of the perfume.

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D3/50 C11D3/12 C11D17/00 A61K7/46 A61K7/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 521 635 (UNILEVER) 7 January 1993 see page 5, line 33 - line 35; claims; examples ---	1-9
A	EP,A,0 535 942 (UNILEVER) 7 April 1993 cited in the application see examples ---	1
A	EP,A,0 149 264 (UNILEVER) 24 July 1985 see example 7 ---	1
P,X	EP,A,0 684 301 (PROCTER & GAMBLE) 29 November 1995 see examples -----	1-9

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

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